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DETERMINATION OF MAJOR AND MINOR ELEMENTS IN FUSED COAL ASH SAMPLES WITH ENERGY DISPERSIVE X-RAY SPECTROMETRY USING A FUNDAMENTAL PARAMETER APPROACH

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INTRODUCTION

The rapid quantitive determination of the major and minor elements in coal ash is essential to the efficient utilization of coal in industrial processes, such as power generation, industrial heating and the production of metallurgical coke for the steel industry. Present day energy dispersive X-ray fluorescence spectrometers are well suited to this approach as they can be used for the simultaneous determination of a large number of analytes. However, before a coal ash may be subjected to analysis by XRF, the ash itself must be prepared by standard procedures for presentation to the spectrometer. Ideally, a method of preparation which is both precise and accurate is required. The Solid Fuels Analysis and Standardization Laboratory is now convinced that fusion of a given amount of coal ash with a larger amount of lithium tetraborate flux results in a homogeneous solid solution in which particle size and contamination from grinding agents are eliminated, as are known to occur in other sample preparation techniques, for several reasons:

Firstly, coal ashes tend to vary widely in mineralogical composition and in most cases contain significant amounts of aluminum and silicon which are low Z (low atomic number) analytes. For this reason significant particle size effects are likely to be encountered, as other authors have pointed out (1,2). The particle size effects, generated by differences in mineralogical composition and the presence of low Z analytes can only be removed by grinding to submicron particle size which is difficult to accomplish without contamination from the grinding elements, eg. tungsten. Consequently fusion of coal ash with lithium tetraborate, which eliminates these particle size effects, would seem to be more practical than the powder pellet method, which can never entirely eliminate particle size effects.

Secondly, coal ashes tend to cover wide ranges of concentration of the major elements, therefore, one would expect to encounter large absorption enhancement or matrix effects which are a function of all elements present in a given sample. Fusion of a coal ash tends to "dilute"

these matrix effects. In the powder pellet method the absorption and enhancement effects are not "diluted" by a flux although addition of a binder might dilute these effects slightly.

Although lithium tetraborate "dilutes" the matrix effects especially for light analytes such as magnesium, aluminum, and silicon, the interelement effects may still remain substantial for such analytes as calcium, titanium, and iron. One technique used to virtually eliminate the matrix effects for these analytes is to employ "heavy absorbers" such as La_2O_3, Ce_3O_4, BaO, or WO_3 (3,4). The use of heavy absorbers in a fusion technique to eliminate absorption enhancement effects is not compatible with energy dispersive methods, because in most cases certain fluorescent peaks from the heavy absorber overlap an analyte line of interest and cannot be separated from the analyte line. Some authors have indicated that significant variations in the fluorescence intensities of some analytes from replicate glass disks prepared with lithium tetraborate, heavy absorber and sample have been encountered (4,1). On the other hand fusion of a coal ash with lithium tetraborate without a heavy absorber is compatible with energy dispersive XRF techniques, by eliminating peak overlap caused by the use of a heavy absorber. In addition other workers indicate that replicate pellets made from lithium tetraborate and sample only, give practically constant intensities for the analyte lines of interest (5,6).

However, fusion of coal ash with lithium tetraborate, without a heavy absorber creates a situation where matrix corrections are necessary (4,5). The fundamental parameter method (4,5) was employed to correct for absorption effects in "coal-ash glass disks" and was found to apply over wide concentration ranges.

As certified reference standards are not currently available for the analysis of coal ash, it was decided to use synthetic standards for calibration in the analysis of coal ash. It is possible to prepare synthetic standards from high purity chemicals with chemical compositions similar to that of coal ash. It is not possible, however, to use these synthetic standards in a powder form as calibration standards, because the mineralogical (hardness and particle size) differences between high purity chemicals and the ash derived from naturally occurring coals are

virtually impossible to overcome by grinding. Again, lithium tetraborate fusion is the most attractive alternative.

Theory of Matrix Corrections

As previously indicated, fusion of a given amount of a material consisting of a complex matrix such as coal ash, with a relatively large amount of flux such as lithium tetraborate tends to "dilute" the interelement effects especially for low Z analytes such as sodium, magnesium, aluminum, silicon, phosphorous, and sulphur. However, these absorption-enhancement effects may remain substantial for such analytes as potassium, calcium, titanium, and iron. There have been many empirical equations employed by several workers to compensate for the interelement effects encountered in complex chemical matrices. These equations are usually restricted to limited calibration ranges as a result of the uncertainty of the experimentally determined empirical coefficients even when a large number of standards are employed. Fortunately, the matrix effects in fused discs are predominantly due to absorption (1) with enhancement being of minor importance. Absorption can be mathematically compensated for by the use of mass absorption coefficients using a fundamental excitation equation derived from physics.

For smooth homogeneous specimens in the absence of multiple scatter and enhancement effects the fundamental excitation equation for secondary X-ray excitation with primary X-radiation is (9)

$$I_L = \frac{I_o \ \kappa \ C_A \ (\mu/\rho)_A \ \lambda \text{ pri CSC } \phi}{(\ (\mu/\rho) \text{ matrix, } \lambda \text{ pri CSC } \phi + (\mu/\rho) \text{ matrix, } \lambda \text{ line CSC } \Psi)} \quad (1)$$

Where in equation (1)

I_L	Background corrected analyte line intensity
I_o	Incident photon intensity
κ	Constant consisting of fluorescent yield, probability of electron transition, and analyte jump ratio
C_A	Weight fraction of analyte in sample being analysed by spectrometer
$(\mu/\rho)_A$ pri	Mass absorption coefficient of analyte "A" for the incident primary wavelength

(μ/ρ) matrix, pri — Mass absorption coefficient of specimen matrix for the incident primary wavelength

(μ/ρ) matrix, line — Mass absorption coefficient of the specimen for the analyte line's wavelength

$\emptyset$, Ψ — Angle of incident primary beam and emergent analyte beam with sample surface.

There are two major problems which arise from the use of this fundamental excitation equation. First as stated for equation (1) I_L is the background corrected or "net" analyte line intensity. In practice however, it is not possible to directly measure the "net" line intensity for a given analyte with most energy dispersive spectometers currently available because of the background generated by scatter and line interference from the other analytes present in a matrix under the analyte line of interest. Consequently, before any analytical values can be determined for the analytes present in a matrix from the "raw" X-ray line intensities measured by an energy dispersive X-ray spectrometer, the background must be removed from under the analyte lines. Fortunately, there are various background correction methods available which yield "net" (background corrected) X-ray intensities from "raw" (uncorrected intensities).

The second apparent problem with the use of this fundamental equation is that it applies only to excitation by monochromatic primary radiation. The excitation of standards and samples for this work was carried out with a continuum generated by an X-ray tube so that the analyte lines were excited by all primary wavelengths between the short wavelength limit determined by the tube voltage setting and the absorption edge of the analyte. Fortunately, this continuum may in many cases be replaced by a single "effective" or "apparent monochromatic" wavelength having the same primary absorption and excitation efficiency as the primary continuum generated by the X-ray tube (9).

Since the X-ray tube used in the experimental studies was stable, I_o the incident photon intensity for a given analyte was constant. Furthermore, the angles $\emptyset$ and Ψ were fixed and equal for all analytes so that CSC $\emptyset$ = CSC Ψ, and since the value of $(\mu/\rho)_A$, λ pri is also a constant for each analyte, equation (1) reduces to

$$I_L = \frac{KC_A}{(\ (\mu/\rho)\ \text{matrix},\ \lambda\ \text{effective} + (\mu/\rho)\ \text{matrix},\ \lambda\ \text{line})} \qquad (2)$$

Where in equation (2) $K = k\ I_o\ (\mu/\rho)_A$

λ Effective is the "apparent monochromatic" primary excitation wavelength.

For coal ash fused with lithium tetraborate C_A is the weight fraction of analyte "A" in the coal ash glass disc. The matrix consists of the lithium tetraborate flux and each of the analytes in the coal ash. Consequently,

$$(\mu/\rho)\ \text{matrix},\ \lambda\ \text{eff} = C\ \text{flux}\ (\mu/\rho)\ \text{flux},\ \lambda\ \text{eff} + \sum_i C_i\ (\mu/\rho)_i,\ \lambda\ \text{eff} \qquad (3)$$

$$(\mu/\rho)\ \text{matrix},\ \lambda\ \text{line} = C\ \text{flux}\ (\mu/\rho)\ \text{flux, line} + \sum_i C_i\ (\mu/\rho)_i,\ \lambda\ \text{line} \qquad (4)$$

Where in equations (3) and (4)

C flux Weight fraction of flux in coal ash disc

C_i Weight fraction of analyte i in coal ash class disc.

Combining equations (3) and (4) one obtains

$$(\mu/\rho)\ \text{matrix, A} = C\ \text{flux}\ (\mu/\rho)\ \text{flux, A} + \sum_i C_i\ (\mu/\rho)_i,\ \text{A} \qquad (5)$$

Where in equation (5)

(μ/ρ) matrix, A = (μ/ρ) matrix, λ effective + (μ/ρ) matrix, λ line

(μ/ρ) flux, A = (μ/ρ) flux, λ effective + (μ/ρ) flux, λ line

$(\mu/\rho)_i$, A = $(\mu/\rho)_i$, λ effective + $(\mu/\rho)_i$, λ line

Substituting equation (5) into equation (2) results in

$$I_L = KC_A / (C\ \text{flux}\ (\mu/\rho)\ \text{flux, A} + \sum_i C_i\ (\mu/\rho)_i,\ \text{A}) \qquad (6)$$

However the weight fraction of any analyte in a fused disc is directly related to the weight fraction of the analyte in the original sample by equation (7)

$$C_i = \frac{W\ \text{ash}}{W\ \text{ash} + W\ \text{flux}} \times C'_i = df\ C_i' \qquad (7)$$

Where in equation (7)

W ash is the weight of ash used to prepare the coal ash glass disc.

W flux is the weight of flux used to prepare the coal ash glass disc.

$df = \frac{W\ \text{ash}}{W\ \text{ash} + W\ \text{flux}}$ is the dilution factor

C_i' is the weight fraction of analyte i in the coal ash

And for the flux

$$C\ flux = \frac{W\ flux}{W\ ash + W\ flux} = 1-df \qquad (8)$$

Substituting equations (7) and (8) into (6) one obtains

$$I_L = df\ K\ C_A' / ((1-df)\ (\mu/\rho)\ flux, A + df\ \Sigma\ C_i'\ (\mu/\rho)_i, A) \qquad (9)$$

In equation (9) if

$$g_A = ((1-df)\ (\mu/\rho)\ flux, A + df\ \Sigma\ C_i'\ (\mu/\rho)_i, A) \qquad (10)$$

Then one obtains

$$I_L = df\ KC_A' / g_A \qquad (11)$$

In equation (11) g_A is the absorption factor for analyte "A". This absorption factor can be readily calculated for any standard of known composition from tables of mass absorption coefficients. To calibrate an X-ray spectrometer for each of the ten analytes normally encountered in coal ash one standard could be chosen as a reference standard and the intensity of each analyte line in the reference standard experimentally measured. The intensity of each analyte would also be measured for several other standards. The relative background corrected intensity of each analyte is calculated according to equation (12) below

$$R_A = \frac{I_L\ Stnd}{I_L\ Ref} \qquad (12)$$

Where in equation (12)

I_L Stnd — Background corrected analyte line intensity of a given standard

I_L Ref — Background corrected analyte line intensity of the reference standard.

However, it is evident from equation (11) that

$$I_L\ Stnd = df\ K\ C_A'\ Stnd / g_A\ Stnd$$

$$I_L\ Ref = df\ K\ C_A'\ Ref / g_A\ Ref$$

$$\therefore\ R_A = \frac{I_L\ Stnd}{I_L\ Ref} = \frac{df\ K\ C_A'\ Stnd \times (g_A\ Ref)}{df\ K\ C_A'\ Ref \times (g_A\ Stnd)} = \frac{C_A'\ Stnd \times g_A\ Ref}{C_A'\ Ref \times g_A\ Stnd} \qquad (13)$$

Solving equation (13) for C_A' gives

$$C_A' \text{ Stnd} = C_A' \text{ Ref} \quad R_A \times G \tag{14}$$

Where in equation (14)

C_A' Stnd — weight fraction of analyte "A" in a given standard

C_A' Ref — weight fraction of analyte "A" in the reference standard

$G = (g_A \text{ Stnd}/g_A \text{ Ref})$ is the absorption "correction" factor

Now equation (14) can be rewritten to give

$$C_A'' \text{ Stnd} = C_A' \text{ Ref } R_A \tag{15}$$

$$\left(C_A'' \text{ Stnd} = C_A' \text{ Stnd}/G\right)$$

C_A'' Stnd may be referred to as the "apparent" concentration of analyte "A" in a given standard. This is the concentration of analyte "A" that the X-ray spectrometer appears to "see".

It is obvious that the "apparent" concentration of analyte "A" depends upon the value of the absorption correction factor. This ratio in turn is calculated as indicated above by dividing the absorption factor of a given standard for analyte "A" by the absorption factor of the reference standard for analyte "A". As previously mentioned, it is very simple to calculate the absorption factor for any standard of known composition and consequently the absorption correction factor G. Therefore, the "apparent" concentration of analyte "A" can be calculated for all standards used in the calibration of an X-ray spectrometer. Furthermore, equation (15) is of the form $y = mx$.

Therefore, a linear least-squares fit of the "apparent" concentractions of analyte "A" in a series of standards should give a calibration line with a slope equal to the concentration of analyte "A" in the reference standard passing through the origin. Actually, since commercially available X-ray spectrometers are not completely stable, the calibration line will, in most cases not pass exactly through the origin so that equation (15) becomes

$$C_A'' \text{ Stnd} = C_A' \text{ Ref } R_A + b \tag{16}$$

Where in equation (16)

b is the y intercept due to short term oscilliations (instrumental instability)

With the foregoing arguments in mind, an X-ray spectrometer can be calibrated for the ten major analytes present in coal ash according to the following considerations. As pointed out in equation (10)

$$g_A = ((1-df) (\mu/\rho) \text{ flux, A} + df \Sigma C'_i (\mu/\rho)_{i, A})$$

Now for all standards used in the calibration of an X-ray spectrometer

$$(1-df) (\mu/\rho) \text{ flux, A} = \Theta \qquad (17)$$

where Θ is a constant provided the same weight of ash and flux is used to prepare all standards

As a result equation (10) becomes

$$g_A = (\Theta + df \Sigma C'_i (\mu/\rho)_{i, A}) \qquad (18)$$

Using equation (18) as a guideline 3 situations can occur

Case (a)

$\Theta >> df \Sigma C'_i (\mu/\rho)_{i, A}$ for all standards used in the calibration of a given analyte "A".

In this case

$$g = (\Theta + df \Sigma C'_i (\mu/\rho)_{i, A}) \simeq \text{constant}$$

Then $G = (g \text{ Stnd} / g \text{ Ref}) \simeq 1$ for all standards

And $C_A'' \text{ Stnd} = C_A' \text{ Stnd}/G = C_A' \text{ Stnd}/1 = C_A' \text{ Stnd}$

Case (b)

$\Theta < df \Sigma C'_i (\mu/\rho)_{i,}$ for all standards used in the calibration of a given analyte "A", and $df \Sigma C'_i (\mu/\rho)_{i, A} \simeq$ constant

Again in this case

$$g = (\theta + df \Sigma C'_i (\mu/\rho)_{i, A}) \simeq \text{constant}$$

Then $G = (g \text{ Stnd} / g \text{ Ref}) \simeq 1$ for all standards

And $C_A'' \text{ Stnd} = C_A' \text{ Stnd} / G = C_A' \text{ Stnd} / 1 = C_A' \text{ Stnd}$

Obviously, then in both cases, (a), and (b) the apparent concentration of analyte "A" for all standards would be for all practical purposes equal to the "actual" analyte concentration present in the standard.

i.e., $C_A'' \text{ Stnd} = C_A' \text{ Stnd}$

In this situation equation (16) becomes

$$C_A' \text{ Stnd} = C_A' \text{ Ref } R_A + b \qquad (19)$$

Equation (19) states that for the situation where $g_A \simeq$ constant for all standards as described in cases (a) and (b) above it should be possible to calibrate an X-ray spectometer for analyte "A" by a linear least squares fit of actual analyte "A" concentration against relative background corrected X-ray intensity without having to apply absorption corrections.

Case (a) described above should occur for low Z analytes in lithium tetraborate flux such as Na, Mg, Al, Si, P and S.

Case (b) described above may occur for heavier analytes such as K, Ca, Ti, and Fe for a given set of standards. However, this can only be verified by a linear least squares fit of actual analyte concentration against relative background corrected intensity.

Case (c)

$\Theta < \text{df } \Sigma\ C_i' (\mu/\rho)_{i,A}$ for all standards used in the calibration of a given analyte "A" and $\text{df } \Sigma\ C_i (\mu/g)_{i,A} \neq$ constant.

Then

$$G = \frac{g \text{ Stnd}}{g \text{ Ref}}$$ would result in $G < 1$ or $G > 1$ in most cases

Consequently, the "apparent" analyte concentration would not be equal to the "actual" analyte concentration in a given standard since

$$C_A'' \text{ Stnd} = C_A' \text{ Stnd } / G$$

Therefore, in such a case equation (16) remains

$$C_A'' \text{ Stnd} = C_A' \text{ Ref } R_A + b \qquad (20)$$

Equation (20) implies that for the situation where $g_A \neq$ constant for all standards it is possible to calibrate an X-ray spectrometer for analyte "A" only by a linear least squares fit of "apparent" analyte "A" concentration against relative background corrected intensity. In order to carry out this procedure, it is obviously necessary to apply absorption corrections by calculating "apparent" analyte concentration from "actual" analyte concentration by the use of standard compositions and tables of mass absorption coefficients.

The case discussed above may occur for analytes in lithium tetraborate flux such as K, Ca, Ti, and Fe.

It is evident then, that in order to obtain analytical values for the analytes present in a complex chemical matrix such as coal ash using X-ray spectometry it is necessary to carry our background corrections for all analytes present in the ash and absorption corrections for some of the analytes.

To determine whether the correction methods employed yield acceptable analytical values, the concept of residual scatter as discussed elsewhere (8) was utilized, where

$$Rc = \sqrt{\frac{\Sigma(Caccept - Ccalc)^2}{n-p}} \qquad (21)$$

Wherein equation (21)

Rc is the residual scatter

C calc is the calculated concentration for a specific analyte in a given standard determined from a calibration curve of a linear least squares fit of accepted analyte concentration against relative X-ray intensity, using a given correction procedure.

In the context of this paper, the number of parameters determined by all correction procedures was 2. These were the slope and the y intercept of the calibration line. Therefore, equation (21) reduces to

$$Rc = \sqrt{\frac{\Sigma(C\ accept - C\ calc)^2}{(n-2)}} \qquad (22)$$

Two important facts are evident from equation (22). First, at least 3 standards are required for calibration of any analyte. Second, for any given number of standards Rc will reduce in magnitude as the differences between the accepted value of the standards and the values calculated from a given calibration curve derived using a specified correction procedure become smaller.

Consequently, a reduction in the residual scatter after the application of a correction procedure would be an indication that the correction procedure is most likely valid.

EXPERIMENTAL

Preparation of Standards

Spex hi-pure chemicals (Spex Industries, Metuchen, N.J., U.S.A.) were used to prepare all synthetic standards. The compounds used to prepare the synthetic standards were

Na_2SO_4, MgO, Al_2O_3, SiO_2, KH_2PO_4, K_2SO_4, $CaCo_3$, $CaSO_4$, TiO_2, and Fe_2O_3.

Before use all the materials listed above were dried at 110°C to constant weight except for the $CaCO_3$ which was dried at 260°C. The chemicals were ground to a fine powder in an agate mortar. X-ray intensities of glass disks manufactured from each material before and after grinding showed no evidence of contamination from this grinding procedure. Sixteen synthetic standards were prepared to cover the concentration ranges of the ten major analytes normally encountered in coal ash.

The synthetic standards were prepared by weighing known amounts of the compounds listed above together to give 1 gm. of standard. The standard was then immediately prepared for XRF analysis according to the fusion procedure described below for all samples.

Sample Preparation

All unknown samples were air dried, ground to pass a #60 sieve and ignited at 750°C for 12 hours in a muffle furnace under oxidizing conditions. The resulting "ash" was ground in an agate mortar to pass #200 (0.074mm) sieve. The minus #200 sieve "ash" was then reignited at 750°C to constant weight and prepared for XRF analysis according to the fusion procedure described below.

Fusion Procedure

1. Equipment and Materials

The materials and equipment required for the preparation of standard and coal ash glass discs follow:

(a) Hotplate, capable of maintaining a temperature of 250°C ± 25°C

(b) Muffle furnace, capable of maintaining a temperature of 1050°C ± 50°C.

(c) 95% Pt./5% Au non-wetting crucibles of at least 25 ml. capacity plus 95% Pt./5% Au flanged molds (claisse fluxer) with an I.D. of 32 mm.

(d) Lithium tetraborate flux. As detailed elsewhere (6,7) when lithium tetraborate is fused at high temperatures certain volatiles are expelled resulting in a weight loss of the tetraborate. This loss in weight has been found to be virtually constant for a given lot of $Li_2B_4O_7$, but can vary considerably between different lots of tetraborate (6). Therefore, in order to produce glass discs from different lots of tetraborate which will contain the same amount of this flux it is necessary to compensate the weight of tetraborate used in the fusion procedure for the loss on fusion described above. The compensated weight of lithium tetraborate flux to be used for the fusion procedure is given in the equation below.

$$\text{Compensated weight} = \frac{450 \times Ws}{100 - LOF}$$

Where Ws is the weight of sample, LOF is % loss on fusion of $Li_2B_4O_7$ at 1050°C ± 50°C.

2. Detailed Procedure

(a) Into a clean dry preweighed "non-wetting" platinum crucible transfer 4.5000 ± 0.0001 gms. of $Li_2B_4O_7$ compensated for loss on fusion at 1050°C.

(b) Into the same crucible weigh 1.0000 gms. ± 0.0001 gms. of standard or sample.

(c) Stir the contents of the crucible with a glass stirring rod.

(d) Place the crucible and contents in a muffle furnace which has been preheated to 1050°C ± 50°C.

(e) Swirl the melt in the crucible after 5 minutes and every 15 minutes thereafter until a total of 1¼ hours of fusion time has elapsed.

(f) Remove the crucible and melt from the furnace and allow to cool to room temperature. Weigh the crucible and melt to determine loss on fusion (LOF) of the sample. Place the crucible and contents back in the muffle furnace, and allow to remelt.

(g) Place a "non-wetting" platinum mold in the muffle furnace and allow the mold to reach a temperature of 1050°C ± 50°C.

(h) Pour the melt from the crucible into the mold. Swirl the mold and allow the mold to melt and come to 1050°C ± 50°C.

(i) Transfer the mold to a hotplate at approximately 250°C ± 25°C, and allow the mold to cool on the hotplate for 10 minutes.

(j) Remove the mold to a heat resistant surface and allow the mold to cool to room temperature.

(k) Remove the "glass disc" from the mold.

Experimental Conditions

An Ortec 6110 "TEFA" tube excited fluorescence analyser was used to analyse all glass discs. The analyses were carried out under vacuum using characteristic radiation plus bremstrahlung from a Mo anode X-ray tube operated at 10 Kev anode potential, plus 100 u amp. anode current for 400 seconds. These conditions provided excitation for the analytes listed below.

Na, Mg, Al, Si, P, S, K, Ca, Ti, Fe

To obtain count rates for each of the above ten analytes a "region of interest" centred around the K alpha line of each analyte was set up on the MCA of the 6110 analyser. The start and end channel for each analyte's region of interest or ROI is given in Table 1. Since the gain was set at 10 ev/channel it is possible to compute the Kev equivalent for a given channel. For example, the Kev equivalent of channel 205 is given by

$$\frac{205 \text{ channel} \times 10 \text{ ev/channel}}{1000 \text{ ev/Kev}} = 2.05 \text{ Kev}$$

TABLE 1

ELEMENT	START CHANNEL	END CHANNEL	Kev EQUIVALENTS
Na	102	108	1.02 - 1.08
Mg	122	128	1.22 - 1.28
Al	143	155	1.43 - 1.55
Si	166	182	1.66 - 1.82
P	197	205	1.97 - 2.05
S	222	242	2.22 - 2.42
K	322	340	3.22 - 3.40
Ca	360	378	3.60 - 3.78
Ti	442	460	4.42 - 4.60
Fe	630	650	6.30 - 6.50

RESULTS AND DISCUSSION

Criteria for Calibration of the X-ray Spectrometer and Processing of Data

(All data was processed on a PDP 11/05 computer)

From the sixteen synthetic standards prepared 12 standards were chosen to calibrate the X-ray spectometer for the ten analytes normally encountered in coal ash according to the following procedure:

(1) The "raw" intensities for all ten analytes were measured on the X-ray spectometer for the 12 calibration standards.

(2) One of the 12 calibration standards was chosen as a reference standard.

(3) "Raw" relative intensities were calculated for each analyte in the 12 calibration standards. A linear least squares fit of "actual" analyte concentration against "raw" analyte relative intensity was carried out on the computer. The residual scatter value of the "actual" analyte concentrations determined from the "raw" calibration curve was calculated.

(4) "Background corrections" were applied to the ten analytes in the 12 calibration standards to obtain net analyte intensities from the raw analyte intensities.
A linear least squares fit of "actual" analyte concentration against "net" analyte relative intensity was carried out on the computer. The residual scatter value of the "actual" analyte concentrations as obtained from the "background" corrected calibration curve was determined.

(5) If the residual scatter value calculated from the background corrected calibration curve was significantly less than the residual scatter value calculated from the "raw" calibration curve for a given analyte then the background corrected curve was accepted as the "best" calibration curve for that analyte.

(6) If the residual scatter value calculated from the background corrected calibration showed little or no reduction from the residual scatter value calculated from the raw calibration curve then absorption effects were assumed to be substantial for the analyte in question. In such a case, the X-ray spectrometer could be calibrated only by a linear least squares fit of "apparent" analyte concentration against "net" analyte relative intensity.

The "apparent" analyte concentration can be calculated from standard composition and tables of mass absorption coefficients. For the purposes of this paper mass absorption coefficients from McMaster et al. (11) were employed.

To calculate the "apparent" concentration of a given analyte in each standard it was also necessary to specify an "effective" excitation wavelength. Other authors (9, 10) have indicated that for a given analyte this "effective" excitation wavelength may vary from the analyte's absorption edge wavelength to 2/3 the absorption edge wavelength. As a result, the X-ray spectrometer was calibrated for any analyte for which absorption effects were substantial, employing a computer programme which utilized the following steps.

First, the "apparent" concentration of the analyte in each calibration standard was calculated assuming an "effective" excitation wavelength equal to the wavelength of the analyte's absorption edge. A linear least squares fit of "apparent" analyte concentration against "net" analyte relative intensity was calculated. The residual scatter of the calibration points was determined. The "apparent" analyte concentrations were then recalculated with an "effective" excitation wavelength equal to 80% of the former value. A linear least squares fit was again performed and the residual scatter of the new calibration points calculated. This process was repeated until the effective excitation wavelength became equal to or less than the short wavelength limit determined by the tube voltage setting.

At this point, calculations were terminated. The "absorption" corrected calibration curve which gave the minimum residual scatter was accepted as the "best" calibration curve for the analyte.

Several examples of the effectiveness of the calibration methods discussed above are given below.

Derivation of Net X-ray Intensities

The computation of the "net" (background corrected) X-ray intensities for analytes being determined by energy dispersive XRF analysis can be difficult due to the complex "background" generated in a given analyte's region of interest when a sample contains several analytes.

However, the "background" present in a given analyte's region of interest may be removed by a process known as "stripping." This process necessitates the subtraction of certain "background" data from the raw intensities accumulated in each analyte's region of interest. This data consists of (1) counts contributed by the flux (2) counts contributed by the other analytes in the sample in the form of peak overlap and/or peak tailing, (3) counts contributed by interferring lines from other analytes in the sample matrix.

The "background" counts contributed by the flux to each analyte's region of interest was determined from a pellet made of pure lithium tetraborate. The background counts contributed to a given analyte's region of interest in a sample by peak overlap or low energy tailing from the other analytes present in the sample was determined from pure pellets of each of these analytes. This procedure has been described in other publications (4, 9).

In general, the background contributed by peak overlap or low energy tailing from a given analyte "A" to each other region of interest in a sample will increase linearly with an increase in intensity of analyte "A". This allows the experimenter to establish an analyte "A" background correction constant for each respective region of interest in the sample. In this way, the "background" contribution to a given analyte's region of interest by all other analytes present in a sample in the form of peak overlap and low energy tailing can be calculated.

The analysis of magnesium in coal ash tends to be complicated due to the large amount of background generated in magnesium's region of interest by the flux, peat overlap from aluminum, and low energy tailing from the other analyte peaks in

the coal ash matrix (especially silicon). In fact in most cases, the peak to background ratio is less than unity. Consequently, calibration of an X-ray spectrometer for magnesium regions of interest would yield unacceptable calculated values for magnesium concentrations in the standards used for calibration and a high residual scatter value. However, the removal of the "background" from the magnesium region of interest should improve the calibrated values for magnesium in the standards employed for calibration if the background removal procedures are valid, and a resulting reduction of the residual scatter value should be noted.

Figure 1 illustrates the residual scattering of "actual" MgO concentrations for 12 synthetic standards calculated from a calibration curve of "actual" MgO concentration against raw magnesium relative intensities (closed circles) and calculated from a calibration curve of "actual" MgO concentration against magnesium relative intensities, with the "background" contributed by the flux, peak overlap, and low energy tailing from other analytes (open circles) removed. The slope and y intercept of the calibration curves used to plot the data in Figure 1 is also included. As might be expected, the y intercept for the "background corrected" calibration curve is much closer to zero than the y intercept for the "uncorrected" calibration curve. Notice, however, that due to short term X-ray tube "oscillations" the y intercept for the "background corrected" curve is not exactly zero.

The residual scatter values for the "raw" and "corrected" calibration curves clearly indicate that the background correction method utilized is most likely valid.

"Background" counts in the region of interest of a particular analyte "B" may also originate from the presence of interferring peaks, from other analytes present in the sample. Fortunately, there is a direct relationship between the intensity of the interferring peak of a particular analyte "A" and the intensity of a non-interferring peak of analyte "A". This allows the experimenter to calculate an "interference" constant of analyte "A" for the analyte "B" region of interest, using a pure pellet of analyte "A".

The analysis of phosphorus in coal ash glass discs is especially difficult. As in the case of magnesium there is considerable background generated in the phosphorus region of interest by the flux, peak overlap from sulphur, silicon, and low energy tailing from other analytes in the matrix. In addition,

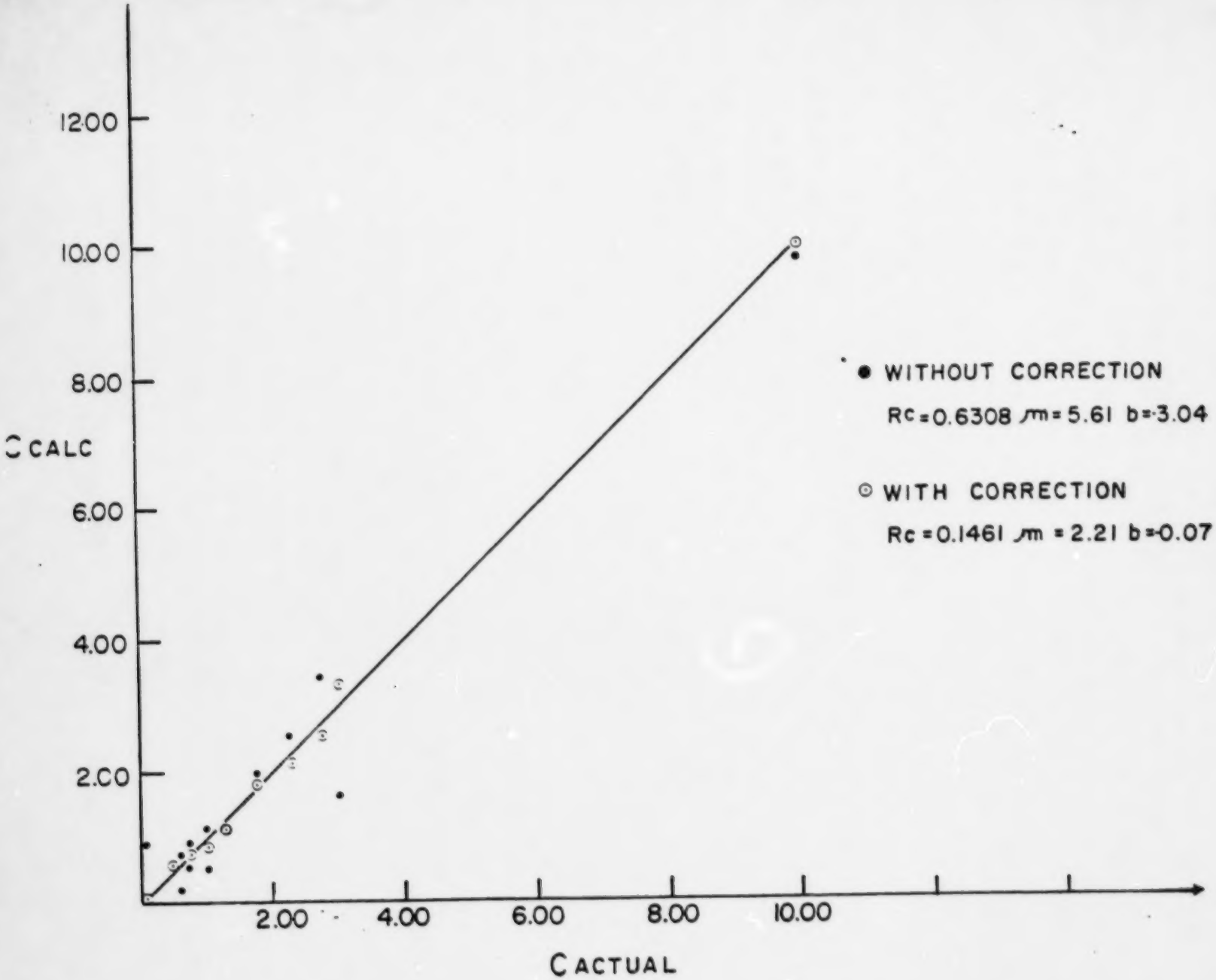

FIGURE 1

MgO Actual Concentration Calculated with and without Background Correction

when a lithium drifted silicon detector is used, there is background generated in the phosphorus region of interest by the calcium "escape" peak.

Figure 2 illustrates the residual scattering of "actual" P_2O_5 concentrations for 12 synthetic standards calculated from a calibration curve of "actual" P_2O_5 concentration against raw phosphorus relative intensities (closed circles), and calculated from a calibration curve of "actual" P_2O_5 concentration against phosphorus relative intensities, with background contributed by the flux, peak overlap from sulphur and silicon, low energy tailing from other analytes, and escape peak interference from calcium removed. In this case, the residual scatter value calculated from the calibration curve derived from "background" corrected intensities is clearly much smaller than the residual scatter value calculated from the calibration curve derived from "raw" intensities, indicating again that the background correction procedure used is probably valid.

Iron, is similar to magnesium and phosphorus in that it also has background generated under its analyte line, however, in the case of iron, the residual scatter value calculated from a calibration curve of "actual" iron concentration plotted against "background" corrected iron relative intensities (R_c = 1.6586) is only slightly less than the residual scatter value calculated from a calibration curve of "actual" iron concentration plotted against "raw" iron relative intensities (R_c = 1.6796).

Clearly then, according to the calibration steps described earlier, one must assume that iron experiences substantial absorption effects in coal ash discs.

Figure 3 illustrates the residual scatter of "actual" Fe_2O_3 concentrations (i.e., uncorrected for absorption effects) for 12 synthetic standards from a calibration curve of "actual" Fe_2O_3 concentration against background corrected Fe_2O_3 relative intensities. Figure 3 also indicates the residual scatter of "apparent" Fe_2O_3 concentrations (i.e., corrected for absorption effects) calculated from the "best" calibration curve for iron as derived by the computer programme. According to the computer the "best" calibration curve for iron occurred for an effective excitation wavelength of 17.43 nm which is in fact, the wavelength of iron's absorption edge.

Table II is a summary of the calibration data for all ten analytes normally encountered in coal ash, for a given calibration run.

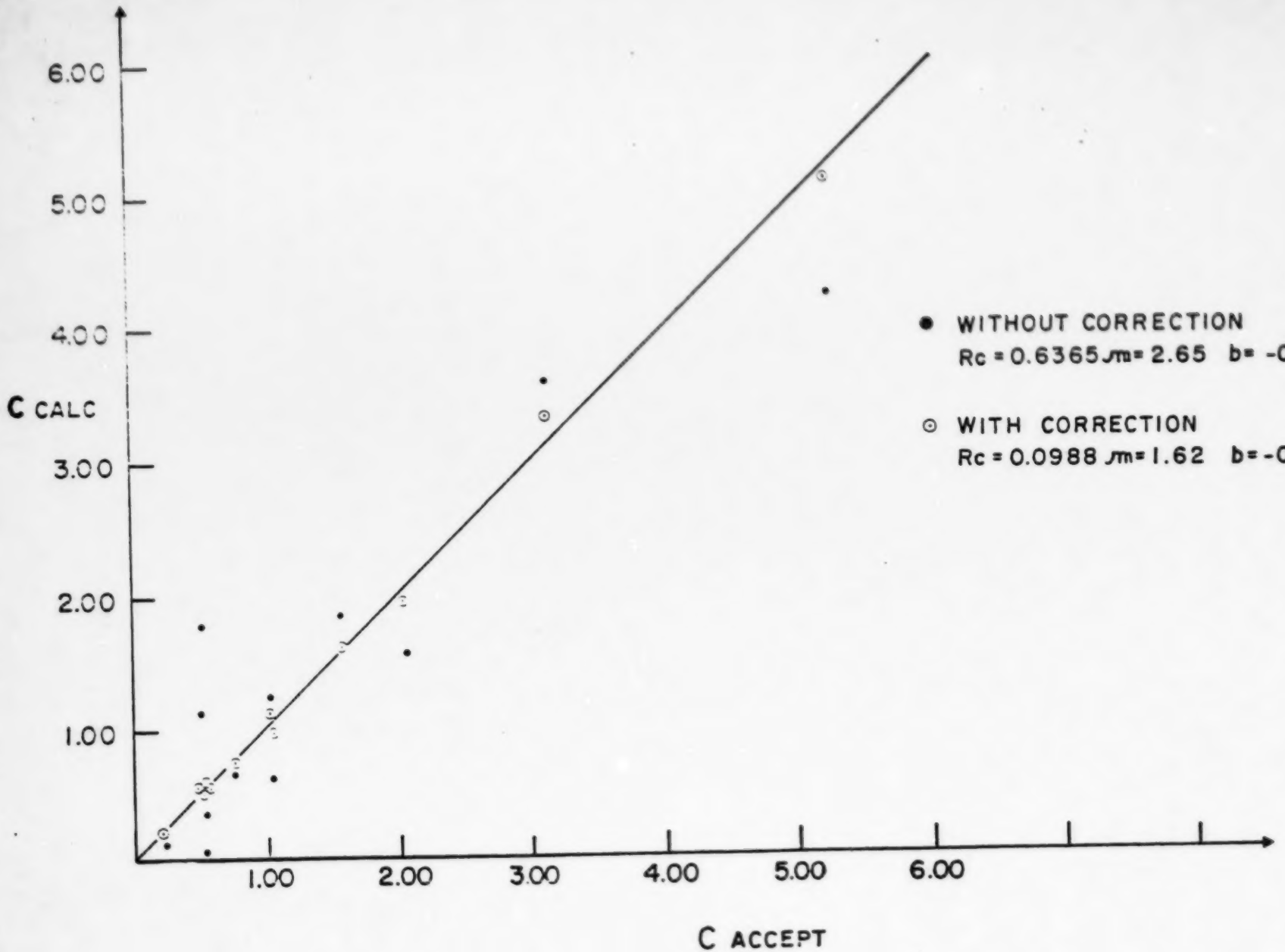

FIGURE 2

P_2O_5 Actual Concentration Calculated with and without Background Correction

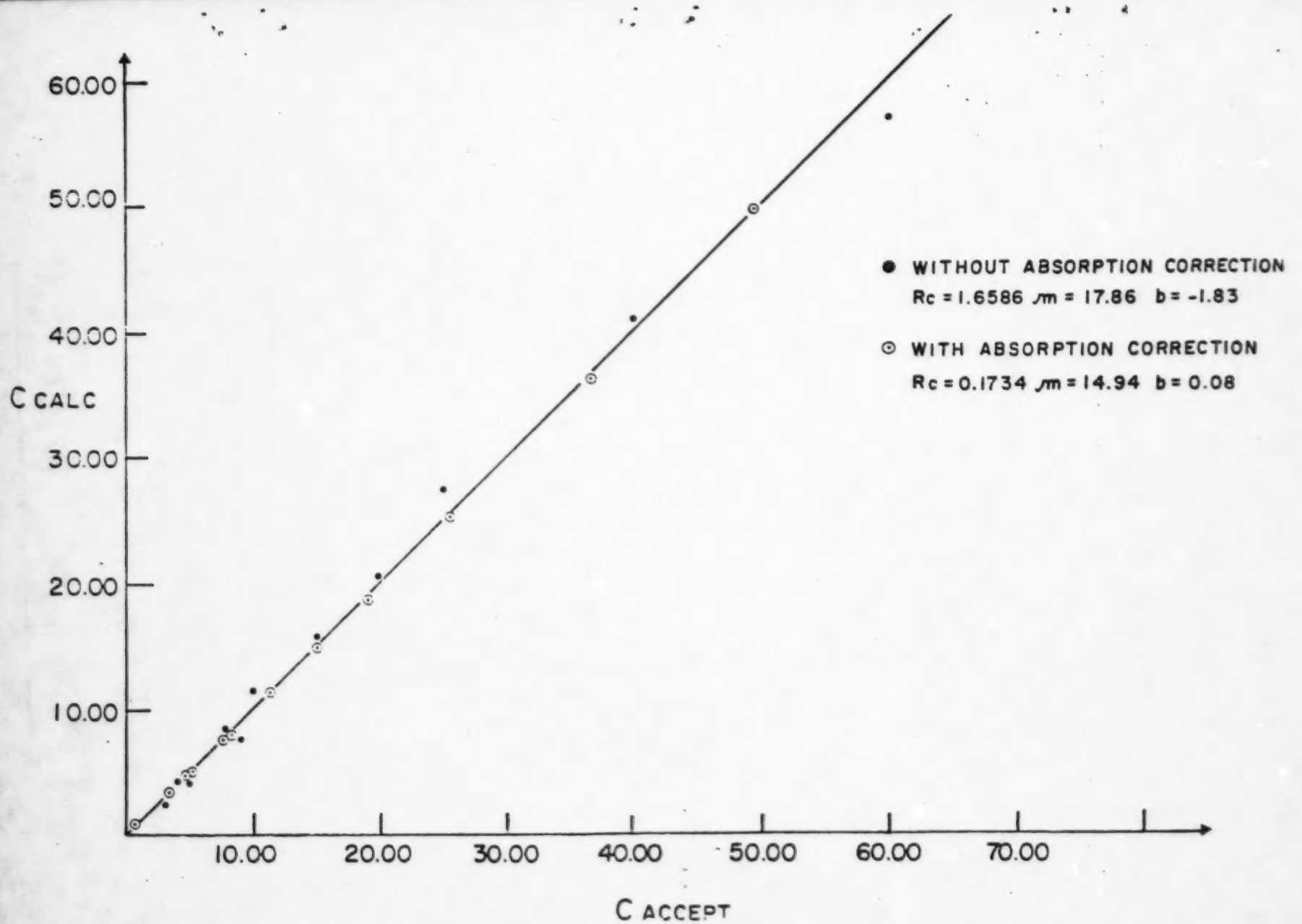

FIGURE 3

Fe_2O_3 Concentration Calculated with and without Absorption Correction

TABLE II

ANALYTE (AS) (OXIDE)	CALIBRATION RANGE WT %	ANALYTE CONC. IN REF. STANDARD	WITHOUT BACKGROUND CORRECTION			WITH BACKGROUND CORRECTION			WITH ABSORPTION CORRECTION				
			Rc	m	b	Rc	m	b	Rc	m	b	λ ABS nm	λ EFF. nm
Na_2O	0.00-8.00	4.00	0.6321	7.09	-3.56	0.4356	4.67	-0.27	N/A	N/A	N/A	N/A	N/A
MgO	0.00-10.00	2.25	0.6308	5.61	-3.04	0.1461	2.21	-0.07	N/A	N/A	N/A	N/A	N/A
Al_2O_3	8.00-40.00	18.00	0.6329	20.29	-2.36	0.3467	17.46	+0.37	0.1992	18.04	-0.24	79.51	63.61
SiO_2	13.00-70.00	30.00	0.9222	30.95	-0.55	0.7575	29.23	+1.08	0.2097	29.42	+0.55	67.45	53.96
P_2O_5	0.26-5.22	1.57	0.6365	2.65	-0.80	0.0988	1.62	+0.04	N/A	N/A	N/A	N/A	N/A
SO_3	0.59-20.11	12.00	0.4554	17.46	-5.95	0.5370	10.98	+0.057	N/A	N/A	N/A	N/A	N/A
K_2O	0.17-7.24	1.04	0.1074	1.49	-0.42	0.0363	1.06	-0.03	N/A	N/A	N/A	N/A	N/A
CaO	0.97-30.00	15.00	0.1629	15.80	-0.65	0.1712	15.26	-0.08	0.0626	14.91	+0.08	30.70	24.56
TiO_2	0.26-4.00	0.93	0.2247	0.99	-0.08	0.1643	0.97	-0.07	0.0387	0.98	-0.03	24.97	19.98
Fe_2O_3	0.50-60.00	15.00	1.6736	18.42	-2.54	1.6586	17.76	-1.84	0.1734	14.94	+0.08	17.43	17.43

The results in Table II illustrate the effectiveness of the background correction methods and absorption correction methods employed in the calibration of the X-ray spectrometer.

For all ten analytes the results without "background" correction yield large negative y intercept values and poor agreement of the calibration curve slope with the concentration of the analyte in the reference standard, indicating the presence of substantial "background" and/or "matrix" effects for all analytes.

Following the application of the background correction procedures described earlier, there is a significant reduction in the residual scatter value, and close agreement between the slope of the calibration curve and the concentration of the analyte in the reference standard for Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5 and K_2O.

Furthermore, for all the analytes mentioned above, there is a substantial reduction in the y intercept except for SiO_2. The improvement in the calibration data for the analytes Na_2O, MgO, Al_2O_3, SiO_2 and P_2O_5 corresponds to Case (a) as described in the theory and consequently the "background" corrected calibration curves for these analytes may be considered acceptable, and the application of absorption corrections is not necessary. The results for the analyte K_2O corresponds to Case (b) in the theory and consequently the "background" corrected curve may be considered adequate for calibration of the X-ray spectrometer for K_2O without application of absorption corrections.

However, for the analytes CaO, TiO_2 and Fe_2O_3, the residual scatter values for the "background" corrected calibration curves are only slightly less than the residual scatter values for the uncorrected calibration curves, indicating that these analytes correspond to Case (c) in the theory and absorption corrections must be applied to these analytes to obtain acceptable calibration curves.

After the application of absorption corrections to CaO, TiO_2, and Fe_2O_3, there is a significant reduction in the residual scatter value for all three analytes and the slope of the calibration curves agrees excellently with the concentration of the analyte in the reference standard. The improvement in the calibration data for these three analytes indicates that the "absorption" corrected curves are acceptable for the calibration of the X-ray spectrometer for CaO, TiO_2 and Fe_2O_3.

It should be also noticed that although not entirely necessary absorption corrections were applied to both Al_2O_3 and SiO_2 with a substantial improvement in

the calibration data (especially for SiO_2). Absorption corrections were applied to these analytes since they tend to cover wide concentration ranges in coal ash. The fact that significant improvements were obtained for the calibration data in situations where the applied absorption corrections were not entirely necessary clearly illustrates the effectiveness of the absorption correction methods. It should be noted that as predicted, the "effective" excitation wavelength for all analytes to which absorption corrections were applied was no less than 2/3 the absorption edge wavelength for the analyte.

It is well to enquire why the residual scatter value for the "background" corrected curve for SO_3 was significantly greater than the residual scatter value for the "uncorrected" curve. Weights taken of the synthetic standard/lithium tetraborate mixtures before and after fusion showed that some standards lost a small amount of weight. This loss in weight was attributed to the loss of small amounts of SO_3 during the fusion procedure making calibration of the X-ray spectrometer for sulphur virtually impossible. Fortunately, the small losses of SO_3 produced only minor errors in the calibration of the spectrometer for analytes where absorption corrections were required.

Experimental Verification

To experimentally verify the applicability of the calibration methods to the analysis of coal ash a large number of samples were presented to the X-ray spectrometer as unknowns. These samples consisted of NBS standards, pure compounds, and round robin coal ash samples. Analyses values for the analytes in these unknowns were calculated, using several sets of calibration curves from different calibration runs. Analytical values determined by X-ray spectrometry were reported for MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO_2, TiO_2 and Fe_2O_3.

Although analytical values for Na_2O were also calculated from X-ray methods, the values were not reported. Na_2O values determined from fused glass discs by X-ray spectrometry are not reliable due to low sodium intensities. SO_3 cannot be determined in fused discs for reasons pointed out earlier.

To obtain analytical values for some analytes in the unknowns, it was necessary to apply absorption corrections. However, the applications of absorption corrections requires a knowledge of the concentration of all analytes in the unknown. In other words, determining the composition of an unknown sample involves using concentrations to calculate concentrations. This may be accomplished using an iterative procedure.

The analytical values for the analytes MgO, P_2O_5 and K_2O in the unknowns were determined directly from their "background" corrected calibration curves without the necessity of absorption corrections and were entered into the unknown composition without further alteration.

Analytical values for the analytes Al_2O_3, SiO_2, CaO, TiO_2 and Fe_2O_3 were calculated using absorption corrections through the following iterative procedure.

(1) "apparent" analyte concentration was calculated from the appropriate calibration curve according to equation (23) for all analytes requiring absorption corrections

$$C_A'' \text{ UNK} = mR_A + b \qquad (23)$$

In equation (23)

C_A'' UNK is the "apparent" concentration of analyte "A" in the unknown.

m is the slope of the calibration curve for analyte "A"

b is the y intercept of the calibration curve for analyte "A"

The "apparent" analyte concentrations calculated for the analytes requiring absorption correction were entered into the unknown composition to give an "initial" estimate of unknown composition.

(2) Using this "initial" estimate of unknown composition the absorption correction factor G for each analyte requiring matrix corrections was calculated and a first approximation of "actual" analyte concentration was calculated according to equation (24) for all analytes requiring absorption correction

$$C_A' \text{ UNK} = C_A'' \text{ UNK} \times G \qquad (24)$$

In equation (24)

C_A' UNK is the "actual" concentration of analyte "A" in the unknown. These "first" estimates of "actual" analyte concentrations were substituted into the initial unknown composition to give a "new" unknown composition.

(3) The G factor for each analyte requiring absorption correction was recalculated using the "new" unknown composition and the "actual" analyte concentration was recalculated to equation (24) to give yet another estimate of unknown composition.

(4) Step (3) was repeated until the change in "actual" analyte concentration

for all analytes requiring absorption corrections was less than a preset value (e.g., 0.10 wt %).

Table III lists the analytical values for the analytes MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2 and Fe_2O_3 as determined by the X-ray methods described in this paper as well as the "expected" results, as determined by a variety of chemical and instrumental methods, for a series of unknown samples.

In general, the agreement between the XRF values as determined by the methods described in this paper with the "expected" values is excellent. However, there are some trends which require explanation. In some instances the TiO_2 values reported in Table III are significantly greater than the "expected" values. In the same cases the Fe_2O_3 values are slightly less than predicted. Qualitative X-ray scans of the samples in which this situation occurred indicated the presence of Barium. On an energy dispersive spectrometer such as the one used for this paper, the Barium L line superimposes itself on the titanium K line and as such acts as an interferring line in the determination of titanium, in that it causes erroneously high results to be reported for titanium. Barium strongly absorbs the iron K line; if the absorption effect of barium is not taken into consideration (which it was not), then slightly low results would be reported for iron.

CONCLUSIONS

The results of this work demonstrate that acceptable analytical values for the analytes MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2 and Fe_2O_3 may be obtained by the X-ray methods described in this paper. Additional work on the effect of the presence of barium on the analytical values determined for titanium and iron is in progress.

TABLE III

SAMPLE DESCRIPTION (IGNITED AT 750°C)	MgO		Al_2O_3		SiO_2		P_2O_5	
	DETERMINED	EXPECTED	DETERMINED	EXPECTED	DETERMINED	EXPECTED	DETERMINED	EXPECTED
NBS-97a	0.00	0.17	44.98	44.75	49.65	50.38	0.45	0.42
NBS-99a	0.00	0.02	20.05	20.50	65.17	65.20	0.00	0.02
USGS-G2	0.51	0.78	15.37	15.41	69.65	69.50	0.10	0.14
USGS-V1	1.56	1.55	17.41	17.49	59.97	59.83	0.49	0.49
Al_2O_3	0.00	0.00	98.47	100.00	-0.46	0.00	0.00	0.00
SiO_2	0.00	0.00	0.00	0.00	99.87	100.00	0.00	0.00
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SRR-168*	1.11	0.99	23.84	24.05	51.39	51.24	0.20	0.20
SRR-137*	0.77	0.83	27.63	27.92	58.14	57.55	0.17	0.18
SRR-135*	1.65	1.36	6.02	6.16	29.33	28.45	0.00	0.14
SRR-169*	0.59	0.48	15.96	18.53	33.85	34.11	0.07	0.11

	K_2O		CaO		TiO_2		Fe_2O_3	
	DETERMINED	EXPECTED	DETERMINED	EXPECTED	DETERMINED	EXPECTED	DETERMINED	EXPECTED
NBS-97a	0.59	0.58	0.23	0.13	2.20	2.19	0.35	0.52
NBS-99a	5.32	5.20	2.11	2.14	0.11	0.01	0.15	0.06
USGS-G2	4.46	4.53	1.95	1.99	0.58	0.54	2.67	2.77
USGS-V1	2.95	2.93	4.85	4.97	1.12	1.05	6.81	6.85
Al_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SiO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.00	0.00	99.59	100.00	0.00	0.00	0.00	0.00
Fe_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	101.50	100.00
SRR-168*	2.42	2.41	2.10	2.12	1.22	1.18	15.42	15.40
SRR-137*	2.04	1.96	0.90	0.84	1.73	1.66	6.49	6.70
SRR-135*	0.60	0.60	50.75	51.87	0.92	0.42	1.56	1.58
SRR-169*	1.45	1.45	1.91	1.94	0.83	0.85	40.56	39.70

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